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PHOTODEGRADATION OF HIGH POLYMERS

PART III - PHOTOLYSIS OF POLY(METHYL METHACRYLATE) IN VACUUM AND IN AIR

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CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL	2
Materials	2
Apparatus	2
Solution Viscosity Measurements	2
Actinometry	3
Product Analysis	4
Procedure	5
RESULTS	5
DISCUSSION	8
Molecular Weight Changes	8
Changes in the Ultraviolet Spectrum of Degraded PMMA	12
Volatile Products	13
Mechanism of PMMA Photolysis	13
Relations Between PMMA and Other Polymers in Degradation	16
SUMMARY	17
ACKNOWLEDGMENTS	17
REFERENCES	18

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ABSTRACT

The photodegradation of poly(methyl methacrylate) films in vacuum and in air by ultraviolet radiation from a medium-pressure mercury lamp has been investigated at room temperature. Changes in molecular weight in terms of intrinsic viscosities, the formation of volatile substances, and the increase in the ultraviolet absorption of the films were followed as a function of energy absorbed. Quantum yields for random chain scission in poly(methyl methacrylate) are about 0.04 and 0.02 in vacuum and in air, respectively. Crosslinking was not observed in air. Quantum yields in vacuum are the same at 2 and 0.02 μ pressure. The quantum yield for methyl formate is approximately that for chain scission; the formate is accompanied by larger amounts of methanol and very small quantities of monomer. Increased ultraviolet absorption occurs after extensive degradation in either air or vacuum and is due to chromophores formed in the polymer rather than in low molecular weight fragments. These observations are rationalized in a mechanism for the photolysis of this polymer.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

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PHOTODEGRADATION OF HIGH POLYMERS

PART III - PHOTOLYSIS OF POLY(METHYL METHACRYLATE) IN VACUUM AND IN AIR

INTRODUCTION

In the outdoor utilization of any organic polymeric material, consideration must be given to the stability of the material to such things as the combined action of atmospheric constituents and sunlight. For most applications, the more energetic wavelengths of radiation from the sun are not a factor in the deterioration of plastics, since such radiation is absorbed by the atmosphere. However, in extraterrestrial use, as in temperature-controlling coatings for space vehicles, polymeric materials in an ultrahigh vacuum will be subjected to solar radiation of very short wavelengths; the consequent degradation would be undesirable from the point of view of both physical and optical properties. From the standpoint of both terrestrial and extraterrestrial application, it is of importance that we know more of the factors involved in the deterioration and stabilization of organic polymers. It is the purpose of this series of reports to describe investigations into the processes of photolytic degradation in high polymers. The ultimate aim of these studies is the stabilization of such materials and the delineation of optimum structural and physical properties for organic polymers under conditions expected in a space environment.

Many parameters are of interest in this research in addition to the wavelength of the absorbed radiation and the exact chemical structure of the polymer undergoing irradiation. The temperature during degradation, the glass transition temperature, and the melting temperature of the polymer may have a profound influence on the diffusion of small fragments through a polymeric film. The effect of traces of oxygen and adventitious photosensitizers in the film must be studied, since these may lead to the absorption of higher wavelengths of radiation and possibly to crosslinking in the film. Crosslinking itself must be investigated, since both desirable and undesirable changes in the physical properties of a polymeric film may result from this effect during irradiation. Finally, the mechanisms for the photolytic degradation of both homopolymers and copolymers under these conditions must be determined and related to both radiolysis and thermal degradation.

Earlier investigations in this field were briefly reviewed in the second report of this series (1). Only a few of these studies were sufficiently quantitative to give quantum yields for either scission of the polymer chain or for the formation of low molecular weight products (2-8). A large variation in temperature and other experimental conditions makes the correlation of results from various laboratories troublesome. At higher temperatures, it may be difficult to separate the photolytic from the thermal processes, the mechanisms of which may differ. If anything, literature reports indicate only that very few generalizations are justified in this field.

The present report extends our earlier study (1) to an investigation of the photolysis of poly(methyl methacrylate) (PMMA) in both vacuum and in air at room temperatures. PMMA was selected for many reasons, not the least of which is that greatly different mechanisms might be expected to predominate at the lower temperature in comparison to that at 160°C. The glass transition temperature (T_g) of this polymer is near 100°C (9), which makes it amenable to study from this standpoint. In addition, analogous polymer structures having a lower T_g can be obtained by using higher esters of methacrylic acid.

A primary reason for the choice of PMMA is that polymethacrylates and polyacrylates are, compared to other vinyl polymers, relatively poor absorbers of ultraviolet radiation, and might thereby be more stable. The effects of crosslinking also may be made more apparent in a comparison of polymethacrylates with polyacrylates, which appear to cross-link readily (4). PMMA has been studied exhaustively from the standpoint of thermal degradation (10) and radiolysis (11), and very recently, Shultz (12) has reported on the photodegradation of PMMA in air under conditions slightly but significantly different from those used here. This report is primarily concerned with the mechanism of the photodegradation of PMMA films in vacuum and a comparison of these results to those from other types of degradation of PMMA as well as to the photolysis of other polymer structures.

EXPERIMENTAL

Materials

Methyl methacrylate monomer was washed with dilute sodium hydroxide solution and distilled water, dried over Drierite, and distilled under nitrogen. Heart cuts were taken, degassed, and immediately polymerized in bulk at 60°C using freshly recrystallized azodiisobutyronitrile as the catalyst. Two batches of polymer were prepared: (a) 100 ml of monomer and 0.1 g catalyst heated 4 hours gave a 30% conversion to PMMA, $[\eta_o] = 1.58$ dl/g in benzene at 30°C after purification, and (b) 200 ml of monomer and 0.011 g catalyst heated 6 hours gave the same conversion to PMMA, $[\eta_o] = 4.54$ dl/g. These polymers were isolated by precipitation with methanol and purified by several reprecipitations from tetrahydrofuran solution with methanol; the bulk polymers were dried in a vacuum oven at 70°C for 60 hours. Intrinsic viscosities of the bulk polymers and blank films prepared from them as described below were identical within experimental error. Tetrahydrofuran was distilled under nitrogen after treatment with lithium aluminum hydride. Redistilled C.P. benzene was used in the viscosity measurements; C.P. methanol and spectroscopic grade methylene chloride were used as received.

Apparatus

The cell and irradiation equipment were similar to that described in the previous report of this series (1). As before, a General Electric Company UA-3 medium pressure mercury lamp surrounded by a quartz water jacket was used as the radiation source. This lamp was mounted approximately 18 inches from the sample cell and, for most work, the overall intensity was reduced to about 10% by inserting calibrated screens between the source and the cell. Runs were made at ambient temperatures.

Spectra were measured with a Perkin-Elmer Spectracord, Model 4000, recording ultraviolet spectrometer. Initial identification of volatile products was made with a Bendix Time-of-Flight mass spectrometer. Other mass spectrometric work was carried out with a Consolidated Electrodynamics Model 21-620 mass spectrometer.

Solution Viscosity Measurements

Viscosities of the polymer samples were measured in benzene solution at $30 \pm 0.01^\circ\text{C}$ using Ubbelohde-type dilution viscometers having running times of about 170 seconds for benzene. Kinetic energy and shear corrections were not made. Intrinsic viscosities, $[\eta_o]$, of the initial polymers as blank films and in the bulk were determined by an extrapolation to zero concentration of plots of η_{sp}/c and $(\ln \eta_{rel})/c$ against c , where c is in grams per 100 ml of solution. From the $[\eta_o]$ and the slopes of the η_{sp}/c vs c plots, the corresponding constants for the Huggins equation were obtained; for $[\eta_o] = 1.58$ and 4.54 these constants

were 0.34 and 0.38 respectively. These constants were unchanged for highly degraded samples of PMMA. Reinsertion of the constants into the Huggins equation gave relations which were used in the single-point determination of the intrinsic viscosity, $[\eta]$, of degraded polymer samples:

$$[\eta] = \left(-1 + \sqrt{1 + 4k \eta_{sp}} \right) / 2c. \quad (1)$$

Post-effects (13) were not studied, but viscosities of samples were run as soon as possible after irradiation.

Viscosity-average molecular weights were calculated from the relation based on light-scattering measurements by Casassa (12)

$$\log \bar{M}_v = (4.102 + \log [\eta]) / 0.73. \quad (2)$$

The polymers used in this work, having $[\eta_0] = 1.58$ and 4.54 , had $\bar{M}_{v_0} = 7.76 \times 10^5$ and 3.31×10^6 , respectively. As noted below, these correspond to $\bar{M}_{n_0} = 3.88 \times 10^5$ and 1.66×10^6 .

Actinometry

Inspection of the ultraviolet spectrum of PMMA (Fig. 1) shows that this polymer presents a difficult actinometric problem, since its absorption is very slight at wavelengths above 2500 Å. For example, at 2537 Å, our thin (about 1.5×10^{-3} cm) films had an apparent absorption coefficient of about 9 cm^{-1} ; for considerably thicker films of PMMA, Shultz (12) found about 18 cm^{-1} , while Cowley and Melville (6) obtained about 37 cm^{-1} for a benzoyl peroxide-initiated PMMA. Of the total light intensity emanating from the UA-3 source, therefore, only a small proportion is actually being absorbed by the polymer sample. Since the method of measurement used in this work is subject to some error, and differences between large numbers are being taken to give the number of quanta absorbed, a high order of accuracy is not claimed for the quantum yields reported here.

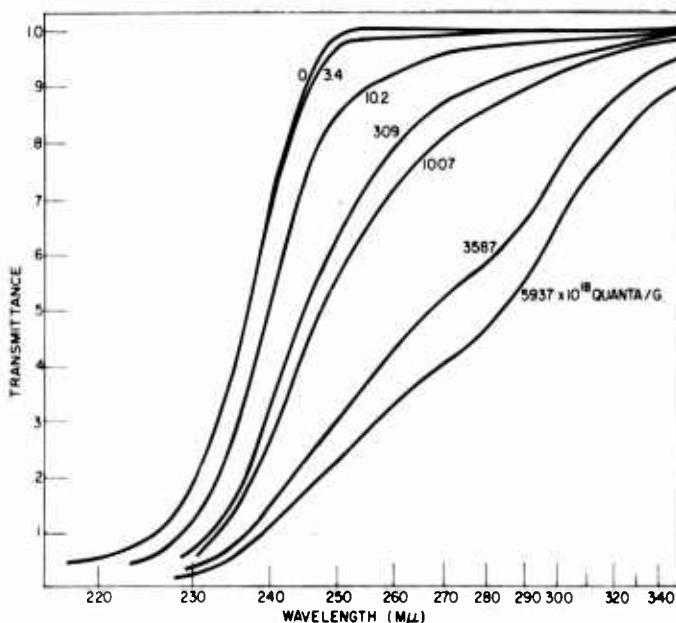


Fig. 1 - Changes in absorption spectrum in PMMA during irradiation

Uranyl oxalate actinometry (14) was used to measure the total output of the lamp from 2200 to 4400 Å. Over a period of several months' intermittent use, the total output of the UA-3 lamp was found to decrease as much as 15%. Actinometer check runs were therefore made for each series of exposures.

The number of quanta absorbed by the exposed films, shown in the tables in the next section of this report, were calculated from the absorption spectrum of the films and the spectral distribution of a typical UA-3 lamp (15). This distribution is shown in Table 1. Of the total radiant energy from this lamp between 2200 and 4400 Å, it was found that 3.5% of the incident light as seen by the actinometer was absorbed by the films used in this work. It should be pointed out that this figure may be questioned on several grounds other than the actinometric determination itself. The spectral distribution in particular is not accurately known and probably constitutes the largest single error, since the distribution may be changing as the lamp is used over a long period. Attempts to determine the spectral distribution by the method of Jortner (16) were unsuccessful due primarily to the necessary approximations in the correction factors involved in the spectrometer itself in measurements at wavelengths below 2500 Å. In general, the possible errors in actinometry will tend to make the quantum yields somewhat larger than reported here.

Table 1
Spectral Distribution of a Typical
UA-3 Lamp (15)

Wavelength (Å)	Energy Emitted (watt)
2200-2300	0.72
2300-2400	0.91
2400-2500	1.51
2500-2600	3.95
2600-2700	2.94
2700-2800	0.33
2800-2900	1.84
2900-3000	1.76
3000-3500	11.09
3500-4000	11.26
4000-4400	9.90
4400-5400	0.82

Product Analysis

Volatile products from the photolyses were measured mass spectrometrically. At the outset of this work, it was expected that considerable quantities of monomer might be formed during the degradation, and therefore chemical analyses for this substance were attempted. Bromometric methods were not applicable to the determination of methyl methacrylate due to the slowness of the reaction. The permanganate oxidation rate method of Brockhaus and Jenckel (17), however, could be used to detect as little as 5×10^{-4} moles of methyl methacrylate. Although a rapidly oxidized degradation product was observed by this method, at no time was monomer detected.

Procedure

Films of PMMA were prepared by weighing about 100 mg of the polymer into flat rectangular quartz or Pyrex dishes of known areas, approximately 50 cm^2 . The samples were dissolved in 10 ml of methylene chloride and the solution slowly evaporated at room temperature over a period of at least 24 hours. After evaporation, the films were maintained in a vacuum oven at 70°C for 16 hours, and for vacuum runs, on a vacuum line at room temperature for at least two hours before sealing off the cell for irradiation. In all vacuum runs, a trap cooled by liquid nitrogen was used to condense volatiles produced during the irradiation period. Air exposures were made in a cell similar to that used for the vacuum runs, but with the top portion of the cell removed. As indicated in the results, the ultraviolet spectra of some films were measured *in situ* before and after exposure.

As soon as practicable after irradiation, the films were dissolved in benzene and the viscosities of the solutions determined.

Film thicknesses were calculated from the weights of the polymer and the area of the dishes, assuming a density of 1.18 g/cc. A plot of film thicknesses from 7 to 100μ against scissions per polymer molecule at a constant exposure time showed these quantities to be inversely and linearly related to each other up to a film thickness of 30μ . Actual film thicknesses used in most of the work reported here were within 10% of 15μ .

RESULTS

The gross features of the photodegradation of PMMA films in vacuum are a rapid decrease in viscosity-average molecular weight, the formation of a small amount of volatile products, and a slow general increase in ultraviolet radiation absorption. Similar results were observed in air exposures, although volatile products were not investigated.

In Fig. 1 is shown the progressive changes in the ultraviolet spectrum of one sample of PMMA ($[\eta_0] = 1.58$) exposed in air. Exposure figures are based on exposure times and are not corrected for the increases in absorption; these exposures represent a considerably greater absorption per gram of polymer than those used in the calculation of quantum yields. Nearly identical changes in the spectrum were observed for slightly smaller exposures in vacuum. The greatest exposure shown here was insufficient to produce a change in the infrared spectrum of the film. Reprecipitation of a film of the higher molecular weight ($[\eta_0] = 4.54$) polymer after absorption of 450×10^{18} quanta per gram showed that the increased absorption indicated by the spectrum of the film was probably due to the formation of new chromophores in the polymer itself. With the lower molecular weight polymer, an exposure of about 150×10^{18} quanta per gram of polymer, which resulted in a moderate increase in ultraviolet absorption, also gave rise to enough scissions per polymer chain that the sample could not be precipitated from a methylene chloride solution with methanol; it could not, therefore, be determined in this instance whether the increased absorption was associated with the degraded PMMA chain or with a relatively small fragment. The formation of a definite absorption band at 2850 Å, as observed in some samples by Shultz (12), is just apparent at the highest exposures.

Initial changes in molecular weight, in terms of the intrinsic viscosities of the degraded films, are independent of the incident light intensity and dependent on the total energy absorbed. This is shown in Table 2 for a ten-fold change in the rate of energy absorption and in data presented below; duplicate runs were made in the intensity experiments.

Perhaps the most obvious effect during photodegradation is the rapid decrease in the intrinsic viscosity of the PMMA films. Data for both air and vacuum are presented in Tables 3 to 5. The number of scissions per polymer molecule is represented by the

Table 2
Effect of Intensity on the Photodegradation of PMMA in Vacuum

Rate Energy Absorption (quanta/g polymer/min)	Absorbed Energy (quanta/g polymer)	$[\eta]$ (dl/g)	$([\eta_o]/[\eta])^{1.37} - 1$ (scissions/polymer mol.)
2.7×10^{17}	7.70×10^{18}	1.390	0.192
28.2×10^{17}	7.70×10^{18}	1.383	0.197

Table 3
Exposures at 2μ Pressure

Weight (mg)	Area (cm ²)	Exposure (min)	$[\eta]$ (dl/g)	$([\eta_o]/[\eta])^{1.37} - 1$	Quanta abs/g polymer
$[\eta_o] = 1.581; I_a = 5.29 \times 10^{14}$ quanta/min/cm ²					
100.0	53.0	3.4	1.572	0.008	0.95×10^{18}
100.0	55.2	7.5	1.497	0.077	2.19×10^{18}
100.0	52.6	15.0	1.466	0.109	4.19×10^{18}
100.0	54.4	20.0	1.412	0.168	5.78×10^{18}
106.7	54.4	28.5	1.390	0.192	7.70×10^{18}
72.9	55.2	25.0	1.313	0.290	10.0×10^{18}
103.3	55.2	120.0	1.147	0.552	33.9×10^{18}

Table 4
Exposures at 0.02μ Pressure

Weight (mg)	Area (cm ²)	Exposure (min)	$[\eta]$ (dl/g)	$([\eta_o]/[\eta])^{1.37} - 1$	Quanta abs/g polymer
$[\eta_o] = 1.581; I_a = 5.29 \times 10^{14}$ quanta/min/cm ²					
107.4	54.4	15.0	1.509	0.066	3.74×10^{18}
105.8	53.0	30.0	1.363	0.226	7.43×10^{18}
110.8	53.0	45.0	1.301	0.306	10.6×10^{18}
99.9	54.4	51.1	1.288	0.325	14.7×10^{18}
$[\eta_o] = 1.581; I_a = 4.93 \times 10^{14}$ quanta/min/cm ²					
89.5	43.6	15.0	1.476	0.097	3.69×10^{18}
92.8	44.4	30.0	1.379	0.199	7.08×10^{18}
91.8	43.6	60.0	1.291	0.320	14.1×10^{18}
83.1	43.6	60.0	1.267	0.354	15.5×10^{18}
$[\eta_o] = 4.54; I_a = 4.93 \times 10^{14}$ quanta/min/cm ²					
107.1	54.4	15.0	4.17	0.124	3.75×10^{18}
95.1	44.0	30.0	3.41	0.480	7.08×10^{18}
83.8	43.2	40.0	3.10	0.688	10.2×10^{18}
84.2	43.7	60.0	2.76	0.983	15.3×10^{18}
91.8	43.7	70.0	2.66	1.081	16.5×10^{18}

Table 5
Exposures in Air

Weight (mg)	Area (cm ²)	Exposure (min)	[η] (dl/g)	($[\eta_0]/[\eta]$) ^{1.37} - 1	Quanta abs/g polymer
$[\eta_0] = 1.581; I_a = 7.40 \times 10^{14}$ quanta/min/cm ²					
107.5	55.2	2.00	1.572	0.008	0.76×10^{18}
106.9	54.4	3.92	1.607	0	1.48×10^{18}
105.4	52.6	5.00	1.581	0	1.85×10^{18}
102.5	55.2	5.65	1.583	0	2.25×10^{18}
107.1	52.6	8.45	1.585	0	3.07×10^{18}
104.1	54.4	10.0	1.559	0.019	3.87×10^{18}
107.1	53.0	15.0	1.533	0.043	5.50×10^{18}
111.0	55.2	20.0	1.485	0.089	7.23×10^{18}
108.0	54.4	25.0	1.452	0.124	9.33×10^{18}
109.3	55.2	29.6	1.436	0.140	11.1×10^{18}
106.2	54.4	37.0	1.351	0.240	14.0×10^{18}
$[\eta_0] = 1.581; I_a = 6.26 \times 10^{14}$ quanta/min/cm ²					
94.3	43.6	5.00	1.574	0.007	1.48×10^{18}
86.6	43.7	12.5	1.545	0.037	3.94×10^{18}
90.9	43.8	30.0	1.491	0.085	9.00×10^{18}
91.0	43.5	70.0	1.351	0.240	21.3×10^{18}
$[\eta_0] = 4.54; I_a = 6.26 \times 10^{14}$ quanta/min/cm ²					
103.9	55.2	10.0	4.070	0.162(0.038)*	3.33×10^{18}
94.6	55.2	30.0	3.370	0.504(0.119)*	10.9×10^{18}
105.5	54.4	60.0	2.925	0.826(0.195)*	19.4×10^{18}

*Figures in parentheses are converted to basis of $[\eta_0] = 1.581$.

quantity $([\eta_0]/[\eta])^{1.37} - 1$. This is based on the assumption of a "most probable" molecular weight distribution both before and after degradation. Then $2\bar{M}_n = \bar{M}_w \cong \bar{M}_v$, and $\bar{M}_{n_0}/\bar{M}_n = \bar{M}_v/\bar{M}_v = ([\eta_0]/[\eta])^{1/\alpha}$, where \bar{M}_n , \bar{M}_w , and \bar{M}_v are number, weight, and viscosity average molecular weights respectively, the subscript zero indicates the initial molecular weight of the sample, and α is the exponent in the Mark-Houwink relation, $[\eta] = KM^\alpha$; in the present instance, α is 0.73 (Eq. 2).

The data in Table 3 and part of Table 4 are for samples from the same batch of polymer run under the vacuum produced by a mechanical oil pump, 2μ , and that obtained with a mercury diffusion pump, 0.01 to 0.02μ . It is apparent that the number of scissions resulting from a given absorption of quanta are the same under the two pressures, and that it would seem unnecessary under our conditions to work with a high vacuum other than where mass spectra of the products are required.

Photolysis in terms of intrinsic viscosity changes is less in air than in vacuum. This is seen from data in Table 5, obtained with the same UA-3 lamp but at two widely separated periods. The first set of data, at the higher effective radiation level, was obtained relatively early in the life of the lamp, when it might be expected that a greater proportion of

the output of the lamp would be in the photolytically effective wavelengths. It is apparent that some sort of an induction period occurs during the degradation of the PMMA, and this induction period was confirmed in several reruns. Such an induction period was not observed under any other set of conditions.

The data obtained at the lower effective radiation level in air involves two batches of PMMA of widely differing initial molecular weights. Scissions per polymer molecule for the higher molecular weight polymer were converted to the level of the lower molecular weight polymer by multiplying by the factor $([\eta_o]/[\eta'_o])^{1/a}$, which in this case is $(1.58/4.54)^{1.37}$ or 0.236. This conversion is based on the assumption of a random scission mechanism for this degradation, which will be demonstrated in the next section. With this conversion, the data from the two polymers are seen to coincide quite well (Table 4). Somewhat poorer agreement between these polymers was obtained in vacuum runs.

Irradiation of a film of PMMA ($[\eta_o] = 4.54$) in air with 10^{20} quanta of Pyrex-filtered radiation per g of polymer produced no change in the viscosity of the sample. Although practically no absorption of ultraviolet radiation by PMMA occurs in the wavelength region (above 3100 Å) transmitted by Pyrex glass, it was thought possible that very small amounts of adventitious sensitizers absorbing in this region could be responsible for degradation or crosslinking. Under the conditions of this experiment, it is evident that such impurities, if present, are not influencing the results of the degradation by shorter wavelength radiation.

Of the volatile products from the photolysis of PMMA in vacuum identified by mass spectroscopy, methyl formate was by far the most prominent if the sample was not heated after irradiation. In addition to methylene chloride (solvent), lesser amounts of hydrogen, methane, carbon monoxide, and carbon dioxide were observed. The evolution of methyl formate from a film at room temperature increased logarithmically with the time of exposure at constant intensity, indicating that the volatilization of this substance, as would be expected, is diffusion-controlled. One sample of PMMA ($[\eta_o] = 1.58$) was heated 4 hours at 110°C , the volatiles analyzed mass spectroscopically, the sample irradiated ($I_a = 4.1 \times 10^{18}$ quanta/g) at room temperature, again heated 4 hours at 110°C , and the second collection of volatiles analyzed. The results in terms of quantum yields are shown in Table 6.

DISCUSSION

Molecular Weight Changes

It is apparent from the data presented in the preceding section that the photolysis of PMMA in either air or vacuum at room temperature is attended by a rapid decrease in the apparent viscosity-average molecular weight without the accompanying formation of monomer and with the generation of only small amounts of other low molecular weight substances. This behavior is that which would be expected from polymer molecules which are undergoing scission at random points along the chains.

Many theories have been developed to explain the kinetics of the reactions of macromolecules undergoing random scission with or without concomitant crosslinking (10,18,19). Shultz (20) has extended some of the statistical theories to the evaluation of quantum yields obtained by the irradiation of polymer films with light; this theory involves the attenuation of the radiation as it passes through successive layers in the film.

We have chosen to treat our data on the basis of a simple model. In the random scission of a polymer chain, the number of scissions, s , should be proportional to the number

Table 6
Volatile Products

Substance	Quantum Yield $\times 10^2$	Moles $\times 10^7$
Methyl methacrylate (before irradiation)	---	7.4
Methyl methacrylate (after irradiation)	20.0	13.6
Methyl formate	14.5	9.8
Methanol	48.3	32.9

of quanta, I_t , absorbed by that chain, where t is time and I is the rate of energy absorption. The proportionality constant, ϕ_s , is the quantum yield in scissions per quantum absorbed:

$$s = \phi_s I_t. \quad (3)$$

It follows that the quantum yield for random chain scission is independent of initial molecular weight. Experimentally, the quantities measured are changes in molecular weight and the number of quanta absorbed by the sample. For polymer chains of number-average molecular weight \bar{M}_{n_0} undergoing random scission, the number of scissions or the number of new polymer chains formed will be $(\bar{M}_{n_0}/\bar{M}_n) - 1$, where \bar{M}_n is the number-average molecular weight after degradation. If a "most probable" molecular weight distribution is assumed before and after degradation, then, as shown earlier in this report, the number of scissions will be equivalent to $([\eta_0]/[\eta])^{1/\alpha} - 1$. Based on the actinometry, spectral distribution of the lamp, and the absorption spectrum of the polymer film, the number of quanta absorbed per gram of polymer, $I_a t$, can be computed. Since one gram of polymer initially contains A/\bar{M}_{n_0} molecules, the quanta absorbed by one molecule of polymer is $I_a t \bar{M}_{n_0}/A$, where A is Avogadro's number. Equation (3) can now be put in terms of experimental quantities by substitution to give

$$([\eta_0]/[\eta])^{1/\alpha} - 1 = \phi_s I_a t \bar{M}_{n_0}/A \quad (4)$$

which on rearrangement becomes

$$\phi_s = \left(A/\bar{M}_{n_0} \right) \left[([\eta_0]/[\eta])^{1/\alpha} - 1 \right] / I_a t \quad (5)$$

from which the quantum yield for chain scission can be evaluated from the slope of a plot of number of scissions against number of quanta absorbed per gram of polymer.

In this way, the data in Tables 3 to 5 have been used to compute quantum yields under various conditions. The plots are shown in Figs. 2 to 4. Quantum yields thus calculated are summarized in Table 7.

Three points are evident from the quantum yields given in Table 7: air apparently acts as a retardant for the scission of PMMA, the spectral distribution of the lamp probably influences the quantum yield, and the number-average molecular weight has little effect on the quantum yield.

As noted earlier, the spectral distribution may be all-important in the quantum yield. This is especially so in view of the fact that practically all of the absorption of ultraviolet light takes place at wavelengths below 2500 Å. As the wavelength decreases, the energy

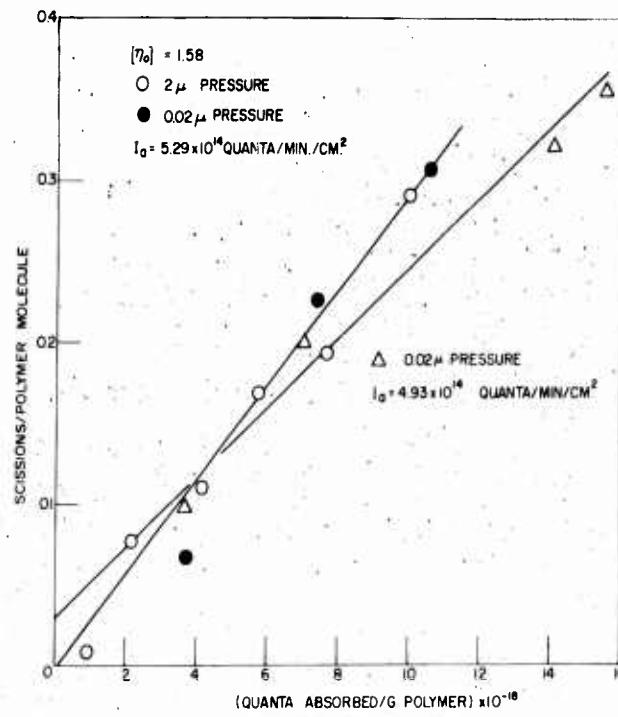


Fig. 2 - Number of scissions vs number of quanta absorbed per gram of PMMA irradiated in vacuum

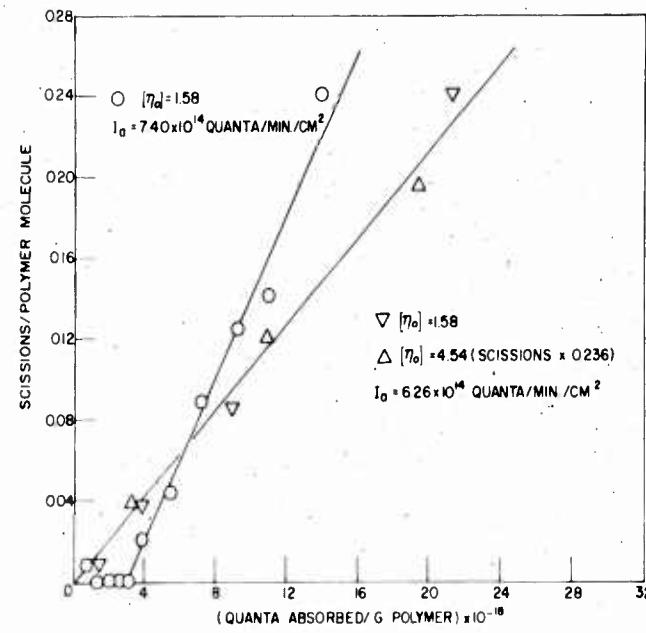


Fig. 3 - PMMA irradiated in air

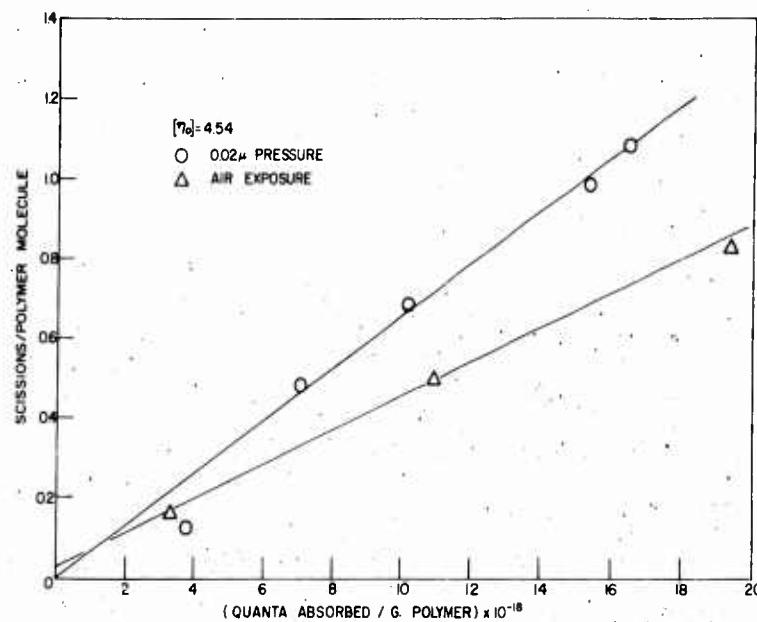


Fig. 4 - Comparison of PMMA irradiated in vacuum and in air

Table 7
Quantum Yields for the Photolysis of PMMA
as Obtained From Figs. 2-4

$[\eta_0]$	Pressure	I_a (quanta/min/cm ²)	Quantum Yield (scissions/quantum)
1.58	0.02 μ	5.29×10^{14}	0.044
1.58	2.0 μ	5.29×10^{14}	0.044
1.58	0.02 μ	4.93×10^{14}	0.024
4.54	0.02 μ	4.93×10^{14}	0.034
1.58	1 atm	7.40×10^{14}	0.018
1.58	1 atm	6.26×10^{14}	0.017
4.54	1 atm	6.26×10^{14}	0.017

per quantum increases, so that it would be expected that the quantum yield may well be determined by the wavelength of the radiation, and it was found that this was so in a qualitative way by comparing a new and old UA-3 lamp by the emission method of Jortner (16). Therefore, as the overall intensity decreases, the quantum yield may also be expected to decrease due to changed spectral distribution of the light source. This is borne out by the results and is further confirmed by comparison to the work of Shultz (12), who obtained 2.3×10^{-3} scissions per absorbed quantum in air with somewhat thicker films of unpurified polymer initiated with lauroyl peroxide. His source was a low pressure mercury lamp, the output of which was essentially 2537 Å radiation, for which the absorption coefficient of the films used was about 19 cm^{-1} (we calculate about

9 cm⁻¹ for our films at this wavelength). Since monochromatic radiation results in more accurate actinometric determinations and avoids spectral distribution influences, Shultz's value is probably quite reliable for 2537 Å radiation.

The role of oxygen in the photodegradation of PMMA is more difficult to assess without considerably more investigation. In addition to involvement in the formation of volatile oxygenated products, oxygen might act as a scavenger at chain radical sites, form carbonyl groups in the polymer chain, or more importantly, may cause crosslinking of polymer molecules. Kilb (21) showed that changes in viscosity are insensitive to crosslinking where the ratio of scissions to crosslinking is greater than 10. Viscosity ratios may either increase or decrease with simultaneous crosslinking and degradation, depending not only on the latter parameters, but also on the solvent used in the determination of viscosity. Both Shultz (11) and Kilb (21), working with Shultz's data on γ -irradiated PMMA, found very little crosslinking. Oster (22) and others (23), on the other hand, found that PMMA in the presence of certain sensitizers was crosslinked upon irradiation with ultraviolet light. Crosslinking was not reported to occur upon irradiation of PMMA either by electrons (24) or by 2537 Å mercury radiation (12). Under our conditions, we did not observe gel formation, and preliminary sedimentation studies with the ultracentrifuge revealed no evidence of crosslinking in highly degraded samples in air.

One criterion for random scission taking place during the photolysis of PMMA is satisfied in the finding of identical quantum yields for scission in samples of polymer differing widely in molecular weight. The values given in Table 7 show that this is the case for air exposures, with somewhat poorer agreement in the vacuum runs. At temperatures where mobility of polymer chains is low, this behavior would be expected and is generally found. In the case of PMMA irradiated at 160°C and above, where diffusion of monomer and other volatiles can more readily take place, end-group attack predominates over random initiation (6). This may be due to acceleration of the thermal degradation processes which proceed by end-group attack and depolymerization, rather than true photolytic degradation.

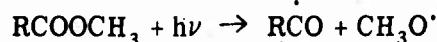
Insight into the termination step in the photolysis of PMMA is provided for by the effect of intensity on the scission of the polymer. From the data in Table 2, it is apparent that the photodegradation of PMMA, insofar as chain scission is concerned, is independent of the intensity of the radiation. This is generally interpreted in the case of gases (25) to mean that the termination step is first order with respect to the radicals involved. Extrapolation to a solid polymer film, admittedly a big step, indicates that recombination of radicals is probably not an important step in the mechanism of the degradation. The combination of mobile, small, possibly reactive, radicals with each other or with a polymer radical would likely be a relatively rapid reaction, while the recombination of less mobile polymer radicals would have a lower probability. It would seem that some sort of a disproportionation reaction of polymer radicals would best describe the slowest termination of radicals in the photolysis of PMMA in our experiments.

Changes in the Ultraviolet Spectrum of Degraded PMMA

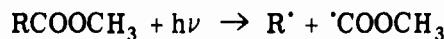
Spectral changes in irradiated PMMA films as seen in Fig. 1 appear to be general increases in absorption with only a hint of an absorption band at 285 mm. This band was observed but not identified by Shultz (12) in 2537 Å-irradiated PMMA films. Other than that the band is in the region of absorption exhibited by the carbonyl chromophore, little can be said. The absorption is definitely associated with the polymer rather than a small molecule unless the latter is highly adsorbed on the polymer even in methanol, which seems unlikely. Conjugated aldehydes absorb at wavelengths longer than 285 m μ , while conjugated esters absorb at shorter wavelengths.

Volatile Products

Of greatest importance is the finding of methyl formate in amounts approximating in quantum yield twice that of the quantum yield for chain scission. This means that there is a fair probability that the formation of a methyl formate molecule is associated with a chain break. Since both monomer and methylene chloride, but only traces of methanol, were evolved on heating the film before irradiation, but all three substances were obtained after irradiation, it can be assumed that the relatively large amount of methanol formed is a product of photolysis rather than residual precipitating medium from the purification of the polymer. It has been noted in the past (1) that irradiation appears to enhance the diffusion of small molecules from a solid polymer. Methanol would be more likely to form as the result of primary photolysis of the ester side groups on the polymer than through photolysis of methyl formate, since the absorption spectra of formate and polymer are similar (PMMA absorbs slightly higher wavelengths) and the amount of formate in the film at any time must be small. The photolysis of the prototype unit of PMMA, methyl pivalate, $(\text{CH}_3)_3\text{CCOOCH}_3$, has not been studied. By analogy with the photolysis of small molecule esters (26-28) a probable primary act after absorption of energy by the ester group would be



or



either of which could lead to many of the products found through secondary reactions or through combination with hydrogen atoms which are surely generated during the photolysis. It is noteworthy that combination of RCO , where R is a polymer chain, with a hydrogen atom leads to the formation of RCHO , an aldehyde, which would be expected to have an absorption maximum with a low extinction coefficient in the vicinity of $285 \text{ m}\mu$.

The observation of a somewhat greater amount of monomer after irradiation than before may mean either that the diffusion rate of monomer has increased as a result of irradiation or that a small amount of depolymerization is occurring after chain scission has taken place. The indicated zip length (kinetic chain length) from the quantum yields in Table 6 is about five monomer molecules per scission. At present, we have no evidence for a chain reaction during photolysis at room temperature. Such a reaction would be quite likely in view of the work of Cowley and Melville (6) at 160°C and higher, where the zip length was at least 220 monomer molecules per quantum absorbed.

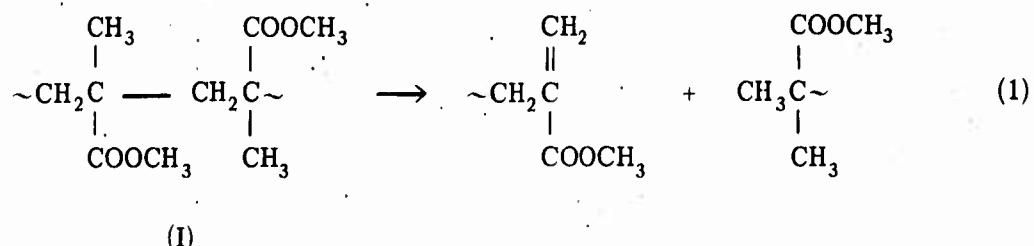
Mechanism of PMMA Photolysis

Any mechanism which may be proposed for the photodegradation of PMMA in vacuum must rationalize the following facts:

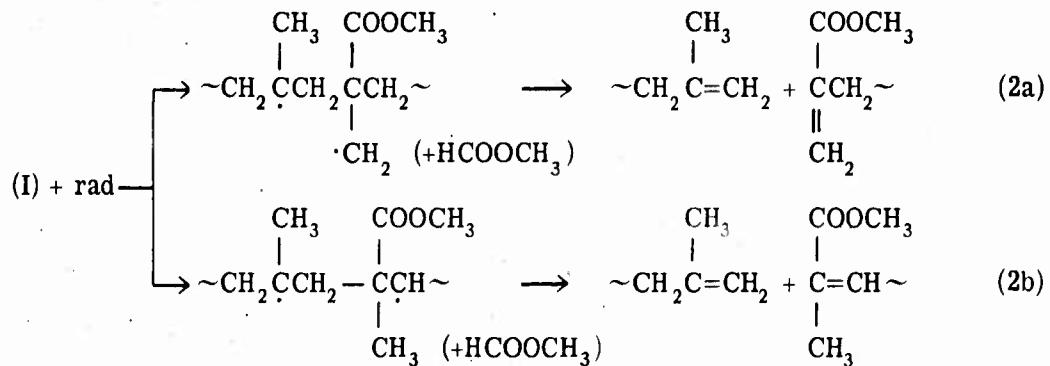
1. Scission of the polymer molecule occurs in a random fashion along the chain. The quantum yield for chain scission in vacuum is higher than that found in air.
2. Termination of polymer radicals is first order in respect to polymer.
3. Approximately two molecules of methyl formate are formed for each polymer chain scission; several times this amount of methanol is formed at the same time.
4. A general increase in absorption in the ultraviolet spectrum, particularly in the $285 \text{ m}\mu$ region, takes place during degradation. This absorption does not appear to be associated with atmospheric oxygen, and it is due to new chromophores in degraded polymer rather than in a small molecule.

At present, it is difficult to draw many conclusions regarding the photodegradation of PMMA in air. Superficially, it resembles that occurring in vacuum except that it appears to proceed at a slower rate. Since the nature of the low molecular weight products, other than by inference from the vacuum work, and the extent to which crosslinking may occur in the presence of oxygen are unknown, oxidative photodegradation of PMMA must remain an area for future investigation.

In addition to simple disproportionation of PMMA:

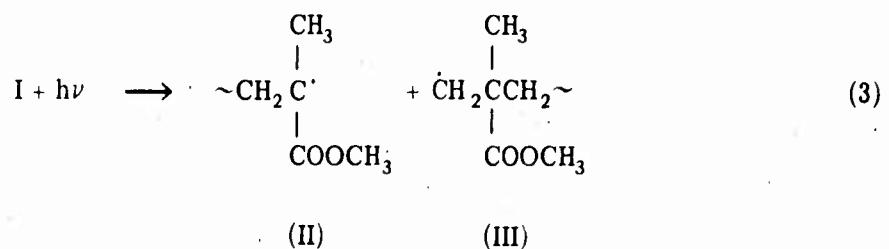


which accounts only for main-chain scission, Shultz (12) proposed for radiolysis a diradical mechanism:

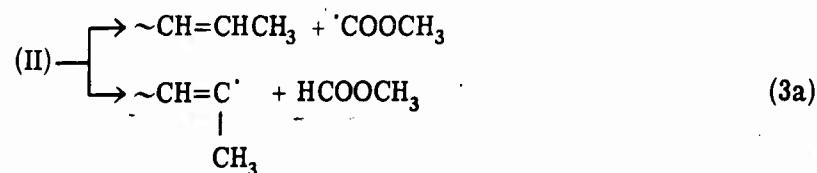


Such a mechanism seems unnecessarily complex, and positive evidence for it in either photolysis or radiolysis is lacking. These reactions do, however, account for the formation of methyl formate in association with a random chain break. Further photolysis of the formate does not seem likely to be sufficient to account for the other products, as indicated above.

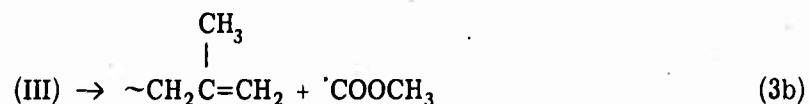
The evidence at hand suggests that at least two and possibly three primary photolytic processes are occurring simultaneously. A major reaction following absorption of energy through the ester chromophore would appear to be homolysis of a main-chain carbon-carbon bond:



followed by stabilization of the resulting radicals, possibly by disproportionation between each other, but more likely through one of the following reactions:

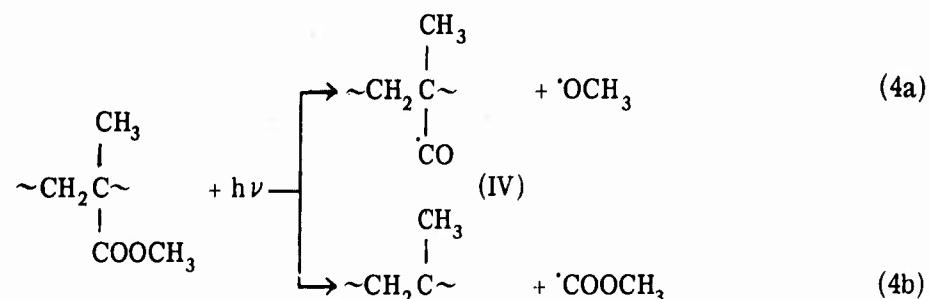


and

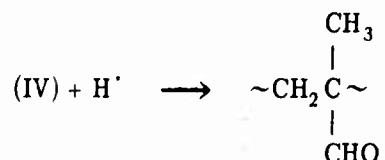


An analysis which distinguishes with certainty between conjugated and nonconjugated olefinic unsaturation in PMMA would help to establish these or the above reactions. In a negative sense, termination by way of these reactions seems more likely than through (1) or (2) in view of our lack of detection of monomer by the permanganate oxidation method (17); this method should detect conjugated unsaturation in the polymer but not isolated double bonds such as those in the chain ends in reaction (3).

An alternative and probably simultaneous reaction is that of photolysis of the ester side chain. By analogy to low molecular weight esters, this may proceed in either or both of two ways, neither of which are necessarily associated with chain scission:



Reaction (4a), of course, could account for the relatively large amount of methanol in the photolysis, and in addition, the termination of IV by combination with a hydrogen atom could give rise to an aldehyde group:



This would account for the $285 \text{ m}\mu$ absorption observed during photolysis. Reaction (4b) could be responsible for the small proportion of methyl formate found in excess of that predicted by the number of scissions.

It should be stressed that the above mechanism has not been established with certainty other than in its broadest aspects. Additional work, as indicated above, will be necessary to give a detailed picture of this photolysis.

Relations Between PMMA and Other Polymers in Degradation

Throughout this report, comparisons have been made between photolysis and radiolysis on the one hand and photolysis and thermal degradation on the other. The case at hand is an excellent illustration of the lack of validity of drawing complete analogies based on work done at temperatures very far removed from those of interest. It is apparent that very different mechanisms are operating at room temperature and at 160°C with PMMA under ultraviolet irradiation. At the lower temperature, random scission with almost no depolymerization occurs, while at the high temperature, end-group attack with much depolymerization is the prevailing reaction. Thus, comparisons of quantum yields for initiation, products, etc., are out of the question, even if radiation sources and polymer structures were identical. By the same token, it is somewhat unfair to compare radiolysis and photolysis of the same polymer under comparable conditions, since there is the strong possibility that radiolysis involves an ionization mechanism rather than a radical reaction. Nonetheless, it is instructive to make some comparisons among the various types of polymer structures which have been examined. With the small amount of quantitative work which has been reported, only vague generalizations are possible.

In Table 8 are listed the approximate G-values for chain scission for a few polymers which have been examined near room temperature. The G-values, in scissions per 100 electron-volts, for photolysis have been computed from the quantum yields and the energy in electron-volts based on an "average" wavelength absorbed. For example, 2300 Å was taken as an "average" wavelength absorbed by PMMA, and this corresponds to 12395/2300 (Ref. 25, p. 15) or 5.39 ev; the G-value of PMMA in vacuum is therefore $100(4.4 \times 10^{-2}/5.39)$ or 0.82 scissions per 100 ev. Only structures of the type $\sim \text{CH}_2\text{C}(\text{CH}_3)(\text{X})\sim$ are shown in the table, since crosslinking enters the picture with polymers containing tertiary hydrogen atoms.

Table 8
G-Values for Chain Scission

Polymer		G-Value (scissions/100 ev)	
		Photolysis*	Radiolysis*
Poly(methyl methacrylate)	Vac.	0.82	1.7 (29)
	Air	0.32 (0.047-12)	1.1 (29)
Poly(methyl isopropenyl ketone)	Vac.	---	1.1 (29)
	Air	4.5 (29)	2.4 (29)
Poly(α -methylstyrene)	Vac.	0.02 (1)	0.25 (30)

*References in parentheses.

It is evident that the order of stabilities in air and vacuum or for photolysis and radiolysis in air are not necessarily the same for various polymers. Of interest are the relative stabilities of the three polymers to photolysis in air: $\text{X} = \text{C}_6\text{H}_5 > \text{COOCH}_3 > \text{COCH}(\text{CH}_3)_2$, with the ketone by far the least stable. The stability of poly(α -methylstyrene) relative to the others is probably due to resonance in the benzene ring. On a time basis, PMMA is also less stable than the poly(α -methylstyrene), apparently as a result of the higher quantum yields at the shorter wavelengths. Further speculation along these lines is not warranted since the data were not obtained under the same conditions.

SUMMARY

Photodegradation of PMMA in vacuum under irradiation by ultraviolet light at wavelengths below 3100 Å gives rise to rapid random main-chain scission with the formation of methanol and approximately two methyl formate molecules per scission, but with slight depolymerization to give monomer. The quantum yield for scission in vacuum is greater than that in air and is the same at 0.02μ and 2μ pressure. The optical properties of PMMA films change during photolysis due to the accumulation of chromophores in the polymer chain. Such chromophores absorb in the carbonyl region of the ultraviolet spectrum and are formed in both air and in vacuum. A mechanism compatible with these findings has been suggested.

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Naval Research Laboratory. Report 5720.
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R. B. Fox, L. G. Isaacs, Suzanne Stokes, and
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